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SULPHUR DIOXIDE REFERENCE MATERIALS

J. K. Taylor, et al

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Final Report

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
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SULFUR DIOXIDE REFERENCE MATERIALS

ABSTRACT

The development of reference materials to serve for quality control and performance evaluation of measurements of sulfur dioxide by the pararosaniline method is described. Powder samples consisting of sodium sulfite dispersed in mannitol can be prepared to evaluate measurements for the concentration levels of ambient interest. The samples are sufficiently stable in routine use, with a service life of at least three months. By the use of a series of five samples of graded sulfite content, measurement errors greater than five percent are significantly detected. A detailed procedure for preparation of the samples is included. Preliminary studies of an alternate method for preparation of quality control samples, by a freeze-drying process are also described.

1. INTRODUCTION

This report summarizes work to develop and produce test materials for quality control of the pararosaniline (PRA) method for measurement of sulfur dioxide in the ambient air. The requirements for such samples include ease and economy of preparation, stability over a reasonable period of time, and above all, the ability to test the performance of the analytical measurements within the limits imposed by the reliability of the method and by practical monitoring considerations.

The requirements outlined above were considered to be met by the use of a series of five samples with equivalent SO_2 contents in the range of 1 to 30 micrograms. The target of five percent for homogeneity and stability over a three-month period was considered to be acceptable. Cost ceilings were not established, but it was understood that unit-cost was an important consideration.

2. PRELIMINARY INVESTIGATIONS

2.1 Dissolved Samples

The simplest approach to preparation of test materials was considered to be by means of liquid samples. Such materials can be easily prepared in large quantities and techniques are available for dispensing accurately measured volumes into ampoules which are automatically sealed.

Experiments were carried out to investigate aqueous solutions containing SO_2 that would simulate the composition of a typical absorber. It is well known that such solutions have limited stability, decreasing in concentration at a rate of about 1.5 percent per day of storage. Accordingly, studies were undertaken to increase their stability.

An attempt was made to preserve SO_2-TCM (tetrachloromercurate) solutions by sealing them in ampoules in a nitrogen atmosphere. The starting solution was carefully deaerated and then sealed into 10-ml ampoules that had been filled with nitrogen which the in-coming liquid displaced. They were immediately sealed while blanketed in nitrogen. However, selected ampoules, analyzed by the PRA method, showed a continued loss of SO_2, amounting to a 20 percent decrease in 11 days.

It has been reported that mannitol is an inhibitor of the decomposition of SO_2 in solution, so this approach was investigated [1]. Three TCM solutions were prepared containing 10 µg SO_2/10 ml. One of these also contained 0.4 percent mannitol. The solutions were analyzed periodically with the following results:

	Loss after 5 days	Loss after 80 days
Control, stored in refrigerator, 4°C	0%	4%
Stored at room temperature	4%	75%
With mannitol, room temperature	4%	75%

It is clear that mannitol was not effective as a stabilizer. Furthermore, the only satisfactory procedure found was storage at reduced temperature which is not feasible. Accordingly, further work to stabilize SO_2 solutions was discontinued, in favor of other approaches.

2.2 Encapsulated Gas

A novel method of preparing SO_2 reference samples, consisting of enclosing the pure gas in precision-bore capillaries, has been described by R. C. Paule [Anal. Chem. 44 1537 (1972)]. The gas is confined between mercury drops in each end of a capillary. so that it is essentially at atmospheric pressure. Tape seals on each end prevent accidental loss of the contents. The volume of the gas is determined by measurement of the capillary bore and the distance between the mercury drops. The technique for preparation and measurement is described in Paule's paper.

Ten tubes were prepared at each of three nominal levels, as follows: 5, 10, and 20 μg SO_2. To analyze the contents, one tape seal was removed and the tube was held vertically with the lower end beneath the surface of 10 ml of TCM solution in a 25-ml volumetric flask. The tape seal was then removed from the upper end, whereupon both mercury and SO_2 flowed into the solution, after which the latter was determined by the PRA method.

Analytical results on 10 tubes selected at random are given in the following table.

Tube no.	SO_2 by measurement μg	SO_2 by analysis μg
1 - 1	4.0	4.22
3 - 2	5.68	5.86
1 - 3	9.62	9.30
2 - 3	9.13	8.70
4 - 3	9.91	10.08
5 - 3	9.34	9.76
2 - 5	20.18	20.70
3 - 5	21.37	21.60
4 - 6	21.86	21.63
6 - 6	21.39	20.68

The results show a good degree of reliability of standards prepared by this technique. Such standards have the advantage of a high degree of simulation with samples collected in the field. The main disadvantage is the relatively high cost of preparation since they must be individually calibrated.

2.3 Powder Samples

The feasibility of producing solid samples containing chemically equivalent amounts of SO_2 was investigated and found to be a satisfactory approach. An initial search was made for a solid inert diluent in which to disperse sodium sulfite. Such a diluent must not only be inert to sodium sulfite or other chemical equivalents of SO_2, but also it should not interfere with subsequent determinations by the pararosaniline method. Because of the earlier experience with mannitol, this was investigated and found to be useful. It was further shown that large excesses of mannitol did not interfere with the PRA method.

Mannitol-sodium sulfite dispersions were prepared in the following manner. ACS reagent grade D-mannitol was put through a fine-mesh screen to break up any lumps. The required amount of powdered sodium sulfite was added and

mixed thoroughly. In the initial experiments, mixing was by ball milling, using plastic balls. This was later replaced by a V-tube blender. Details are given in Section 3.1.

It was originally planned to fix the composition of the mixture so that the analyst could weigh a small portion and dissolve in 10 ml of the TCM solution. A solid mixture consisting of 83.6 mg Na_2SO_3 in 150 g of mannitol was prepared. This mixture is equivalent to 28.3 µg SO_2/100 mg sample. Samples of 50 to 80 mg of this were taken and analyzed with the following results:

Sample no.	SO_2 µg/100 µg
1	23.8
2	34.2
3	16.9
4	23.1
5	33.0
Average	26.2

While the average value was near the expected composition, the deviations between samples were too large. Accordingly, the mixture was twice reblended and analyzed after each trial. Average values of 32.3 µg/100 mg and 29.8 µg/100 mg were obtained, respectively, with between-sample deviations as before. It was concluded that the limit of homogeneity for a 100-mg sample had been reached and that larger samples would be required to achieve the requisite uniformity. To test this hypothesis, four 0.8-g samples were weighed and dissolved in 100 ml of TCM in a volumetric flask. Aliquots of 5 ml and 10 ml were then analyzed with the following results.

Sample no.	5 ml aliquot SO_2, µg/100 ml	10 ml aliquot SO_2, µg/100 ml
1	25.2	26.4
2	25.5	25.4
3	24.0	25.1
4	23.0	23.4
Grand average	24.75	
Standard deviation	1.23	

Three large mixtures were prepared containing 17.0, 30.0, and 7.0 µg SO_2/100 mg and labelled A, B, and C, respectively. These were analyzed initially, and periodically, to investigate their stability. Initial analyses were made on 10 ml aliquots of four 1-g samples which were dissolved in 100 ml of TCM solution. The results are given below:

Sample number-aliquot		Mixture, SO_2, µg/100 mg aliquot A	B
1	a	17.21	31.2
1	b	16.94	31.6
2	a	16.63	29.6
2	b	16.46	30.0
3	a	17.21	29.7
3	b	17.05	30.1
4	a	16.82	30.2
4	b	17.08	30.3
Average		16.93	30.3
2.d.		0.27	1.0

Additional samples from mixtures A, B, and C were analyzed periodically with the following results:

Days after preparation	Mixture, SO_2, µg/100 mg aliquot A	B	C
1	16.9	30.3	7.6
7	16.5	30.2	
10	16.4		
15		30.0	7.0
19	16.6	30.5	
26	16.5		
42		29.3	

The behaviour observed over a 6-week period indicated that the samples would be sufficiently stable during the required three-month period.

3. QUALITY CONTROL MATERIALS

As a result of the foregoing investigation, the quality control materials were chosen to consist of vials containing known amounts of sodium sulfite dispersed in mannitol. To minimize uncertainties due to homogeneity and packaging of fixed amounts of the powders, it is necessary to provide a 1-g sample from which a solution aliquot is then used for the measurement. Two sets of such samples were prepared for EPA. In each case five vials, each containing a specified amount of sodium sulfite (SO_2 equivalent), were provided as a unit of issue. Ampoules of TCM solution were also provided with the first set but were not included in the second because they were deemed unnecessary.

The recommended procedure for use of the samples is as follows. By means of a clean funnel, transfer the contents of a vial into a clean 50-ml volumetric flask with TCM solution. Successive rinses with small volumes of TCM solution are made to insure complete transfer before dilution to

exact volume. The TCM solution is that normally used as a reagent for routine SO_2 sampling. An aliquot of 5 ml of the resulting solution is analyzed for SO_2 in the conventional manner.

The general procedure used at NBS for analysis was as follows. The 5 ml aliquot was transferred to a 25-ml volumetric flask. A 5-ml portion of TCM solution was added. Accurate additions of 2 ml of 0.2 percent formaldehyde solution and 5 ml of pararosaniline solution were made followed by dilution with distilled water to the exact volume. After 30 minutes, the absorbance of the solution was measured at 548 nm, using 1-cm cells, with distilled water as a reference. The SO_2 content was calculated, using a calibration curve prepared in the manner described in the EPA reference method [2].

3.1 Preparation of Samples

The starting materials for each lot were ACS reagent grade chemicals having the following specifications.

D-mannitol

Specific rotation $[\alpha]_D^{25}$	+23.5°
Insoluble matter	0.001%
Residue after ignition	.009%
Loss on drying at 105°C	.004%
Acidity (as CH_3COOH)	.001%
Heavy metals (as Pb)	.0001%

Na_2SO_3, Anhydrous

Assay (Na_2SO_3)	min. 98.5%
Insoluble matter	0.005%
Free alkali (as Na_2CO_3)	.05%
Chloride	.01%
Heavy metals (as Pb)	.001%

The sodium sulfite was ground in a ball mill for seven successive 5-minute periods, with stirring in between. It was then passed through a 60-mesh sieve before use.

Portions of the materials as indicated below were placed in a twin V-shaped dry blender for mixing. Each clear-plastic V-section accepted a charge of about 300 g and rotated at a speed of about 24 rpm. In the rotation process, the contents are alternately divided and combined. The V's were tapped with a wooden block to prevent material from adhering electrostatically to the walls.

Analysis of the blends showed that uniformity had been attained after two hours. The several batches at each level were combined in a large glass jar and intermixed by rotation. Analysis of the individual batches and the total lot showed no significant difference.

The importance of thorough mixing cannot be overemphasized. The critical steps in blending appear to be elimination of all lumps and initial reduction of each component to an equivalent particle size. Anhydrous materials of this kind tend to clump and stick to the walls of the blender, thereby decreasing mixing efficiency. Mechanical shock (tapping the blender) was used to minimize this problem. It is possible that the use of metal vees would overcome this problem but this would not make it possible to observe the mixing and recognize clumping should it occur.

It is also believed to be important to minimize the moisture content of the samples. This is made evident by the increased stability of powder samples over that of solutions. Accordingly, the use of the highest grade chemicals with minimum water content is recommended. Mixing and bottling should be carried out in relatively dry atmospheres and the vials should be stoppered with tight closures.

Batch composition of Lot 1
August, 1972

Series 5000

305.5 g	Mannitol
0.1559 g	Na_2SO_3

Series 4000

305.5 g	Mannitol
0.1217 g	Na_2SO_3

Series 3000

154.9 g	Mannitol
150.1 g	Series 5000 mix

Series 2000

245.0 g	Mannitol
60.0 g	Series 5000 mix

Series 1000

280.0 g	Mannitol
24.6 g	Series 5000 mix

The second lot was made in a similar manner except the concentration levels were changed. Accordingly it was more convenient to make a batch which was used only as a starting material for four of the Series samples.

Batch Composition of Lot II
February, 1974

Bulk Mix

305.5 g	Mannitol
0.156 g	Na_2SO_3

Series 5000

305.5 g	Mannitol
0.075 g	Na_2SO_3

Series 4000

175 g	Mannitol
125 g	Bulk mix

Series 3000

205 g	Mannitol
95 g	Bulk mix

Series 2000

254 g	Mannitol
46 g	Bulk mix

Series 1000

281 g	Mannitol
18.7 g	Bulk mix

The powders were dispensed into 1-oz amber vials using the equipment and facilities of the NBS Office of Standard Reference Materials. A Matur automatic dispensing apparatus was used, provided with a stainless steel hopper and a precision screw dispenser. Check samples were taken at intervals and minor adjustments were made as needed to obtain a uniform weight of sample. The vials were closed with polyethylene insert seals having an inverted hat shape. Aluminum tear-seals were crimped over these to indicate that the vial had not been opened prior to use.

Random samples were selected from each concentration of the production run and were further randomized prior to analysis. Analysis was made by the same procedure as

recommended above. The calibration curve used was obtained by the method described in the Federal Register [2].

3.2 Data on Series I Samples

In addition to analysis for SO_2 content, each of the analytical samples of Lot I was weighed to determine the statistical variation of sample size. The analytical data could then be reported as μg SO_2/100 mg sample.

The data were statistically analyzed by Dr. John Mandel of the NBS. Table 1 is a summary of the statistical analysis. The first grouping lists the average weight, the 95 percent confidence interval for the average, and the standard deviation for the weight of individual bottles. The second grouping lists the average analytical value for a 1/10 solution aliquot, expressed as μg SO_2/aliquot, together with the 95 percent confidence interval for the average and the standard deviation of a single determination. These estimates of error include both analytical uncertainty and variation of composition between bottles, of which the latter is considered to be the major contribution. The values listed in this grouping are those pertinent to the recommended method for use of the samples. The third grouping lists similar information, in which the SO_2 content is calculated on the basis of a given weight of sample. The average assays in the third grouping are larger than those of the second grouping by the factor $\frac{100}{\text{Average Sample Weight}}$. The standard deviations of a single determination are only slightly smaller for the third grouping as compared with the second grouping indicating that the larger source of variation is the homogeneity of the samples, rather than the sample weight. In fact the relation

$$s_{mg\ SO_2/aliquot} = \sqrt{(s_{weight})^2 + (s_{mg\ SO_2/100\ mg})^2}$$

is valid to a high degree.

Table 1. Summary of analytical values, lot I

Series	Weight, g			μg SO_2/aliquot			μg SO_2/100 mg		
	average	95 % c.i. average	s single	average	95 % c.i. average	s single	average	95 % c.i. average	s single
1000	0.934	.014	.029	1.34	.08	.18	1.43	.08	.19
2000	.940	.013	.027	3.94	.19	.40	4.18	.16	.35
3000	.954	.016	.034	11.49	.32	.69	12.04	.27	.57
4000	.938	.017	.035	17.85	.46	.97	19.04	.33	.72
5000	.951	.012	.024	23.02	.46	.94	24.21	.37	.78

NOT REPRODUCIBLE

3.3 Data on Series II Samples

The analytical data for Lot II are summarized in table 2. Because the variation of weight of sample had been found to be of minor significance, the data were analyzed on the basis of μg SO_2/aliquot, according to the recommended mode of use. For some unexplained reason, the variation between samples of the 2000 Series was much larger than that found for the other series. However, this variation should cause no serious problems in the use of the samples for quality control purposes.

Table 2. Summary of analytical values, lot II

Series	n	μg SO_2/aliquot Average	s Single	% cv	$s_{\bar{x}}$	95% c.i. average
1000	10	1.628	0.071	4.4	.022	.05
2000	9	4.034	.335	8.3	.110	
	10	3.904	.254	6.5	.080	
	19	3.966	.294	7.4	.067	.14
3000	10	8.096	.320	3.9	.10	.23
4000	10	10.499	.436	4.2	.14	.32
5000	10	12.197	.242	2.0	.077	.17

3.4 Data on Long-Term Stability

While quality control samples made as described in this report were deemed adequate for short-term use, there was a need to evaluate their long-term stability. Because elaborate storage treatment is not feasible, the useful service life was evaluated under normal conditions, namely in air at room temperature.

Samples were randomly selected from stock and analyzed at intervals over a period of approximately one year with the results given in table 3. Tabulated are the average values found on each date for the number of samples, n, and the standard deviation of the mean, s. It is clear that the samples progressively decreased in SO_2 content. However, the losses are essentially uniform within each series, judged by the reasonable constancy of the coefficient of variation. The average decrease in SO_2 content was 1.4

percent/month for all of the samples except the 1000 series which was approximately twice that value.

Table 3. Stability of series II samples

	2-74			6-74			8-74			1-75	
series	n	average	$s_{\bar{x}}$	n	average	$s_{\bar{x}}$	n	average	$s_{\bar{x}}$	n	average
1000	10	1.628	.022	5	1.229	.057	4	1.099	.054	1	1.046
2000	19	3.966	.067	4	3.572	.172	4	3.412	.145	1	3.268
3000	10	8.096	.100	5	7.780	.122	3	7.393	.104	1	6.765
4000	10	10.499	.140	5	10.121	.268	4	9.909	.302	1	8.595
5000	10	12.197	.077	5	11.365	.380	4	11.623	.271	1	10.098

In view of the progressive but regular decrease of concentration, it would be practical to use the samples for a period of at least one year, provided periodic analyses were made on randomly-selected samples. Alternatively, a method of storage other than in air at room temperature might extend the service life. However, other types of samples should be investigated if long-term stability is a requirement.

4. INVESTIGATION OF FREEZE-DRIED SAMPLES

The feasibility of preparation of quality control samples by a freeze-drying technique was investigated for several reasons. The advantages of dispensing liquid samples have already been mentioned. The freeze-drying of such samples followed by sealing in vacumn or in an inert atmosphere would also eliminate the reaction with air and/or water which is believed responsible for the instability of the powder samples.

Accordingly an experimental lot of freeze-dried samples was prepared for evaluation. A solution of TCM containing 275 µg Na_2SO_3 per ml (equivalent to 139.7 µg SO_2 per ml) was prepared and 0.100 ml aliquots were dispensed into ampoules, using an automatic pipet. The samples were quick-frozen while rotating in an ethanol-dry ice mixture to encourage distribution of the solution as a film on the sides of the ampoule. The ampoules were connected to a vacuum system through a cold-trap, evacuated two hours, and then flame sealed. A total of 45 tubes were prepared in batches of three or four.

Tubes prepared as described above were analyzed periodically over a 10-month period. The results are given in table 4. The within-sample variation of the analytical results, amounts to 0.30 µg. Since this represents both the analytical error and sample variation, the latter is considered to be quite acceptable.

Table 4. Stability of freeze-dried samples

Date	SO_2 found, μg	Average	s
3/18/74	13.36, 13.29, 13.59 13.39, 13.36, 13.19 13.26, 12.96, 13.02	13.27	.19
5/8/74	12.95 13.11, 13.21 13.11	13.10	.11
6/24/74	12.39, 11.47, 11.31 12.19, 11.74, 11.38 11.54	11.72	.42
8/12/74	12.73, 12.76, 12.40 11.65	12.39	.54
1/3/75	12.68, 12.81, 12.39 12.39, 12.52, 12.45	12.54	.17

The apparent changes of composition with time are not readily explainable. It is difficult to believe that the SO_2 decreased and then increased. It is more likely that this represents analytical error. If the results obtained on June 24, 1974 are ignored, the samples can be considered to have experienced a decrease of SO_2 content of about 8 percent/year, but this is only a conjecture.

The freeze-drying technique definitely appears to be a promising approach and merits further study. Equipment is presently available to freeze-dry the contents of vials or ampoules in large quantity and to insert closures under vacuum or inert gas atmospheres. Such a procedure would reduce the cost of preparation of freeze-dried samples.

5. CONCLUSION

A technique has been developed for the preparation of samples suitable for quality control and performance evaluation of sulfur dioxide measurements by the pararosaniline method. Mixtures of sodium sulfite dispersed in anhydrous mannitol can be blended so that 1-g samples have adequate homogeneity for simulating a 24-hour sample at all levels of ambient monitoring. An alternate approach, employing freeze-dried standards, also appears promising.

The purposes of quality control and performance evaluation are best served by the use of multiple samples covering a concentration range. This approach reduces the homo-

geneity requirement for the samples and also provides information on the nature of any analytical error. A single sample can only indicate whether the "right" answer was obtained on that particular sample within its homogeneity limits and the known variance of the measurement system. Statistical considerations make it clear that only relatively large discrepancies will be significant. Dual samples of substantially the same concentration can be used to differentiate between measurement and sample biases but such samples must have compositional uncertainties (inhomogeneity) smaller than the measurement variances. Such samples have the same limitations as single samples in the identification of the source and nature of the analytical error.

The use of several samples, spanning a concentration range provides information on the nature of the analytical error, whether additive or multiplicative. Random variation of individual samples from the lot-average can be tolerated and these can be in excess of the measurement variance, provided a sufficient number of samples is used. The lot-average composition must be bias-free to evaluate the accuracy of a measurement system.

6. ACKNOWLEDGMENTS

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